

Inorganic and Organometallic Chemistry

Joaquim Marçalo

The activities of the Group encompass the synthesis, characterisation and reactivity studies of inorganic, organometallic and intermetallic compounds of the actinides and lanthanides with the aim of understanding the influence of the electronic structure and the size of these elements in the chemical properties of their compounds, and also in an effort to find new applications for the f-elements. Chemical reactivity is assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas-phase ion chemistry and energetics studies, using advanced mass spectrometric and calorimetric techniques, are also undertaken with the same objective.

Important facilities maintained by the Group are a laboratory for catalytic studies prepared for work with CO, a laboratory for handling macroscopic quantities of the more radioactive actinides, a laboratory for calorimetric studies and thermal analysis, and two select mass spectrometers, a FTICR instrument, with EI and LDI sources, and a QIT instrument, with ESI and APCI sources. The QIT mass spectrometer is part of the National Mass Spectrometry Network (RNEM).

Gas-phase chemistry studies were pursued. An overall assessment of the gas-phase energetics of neutral and singly and doubly charged cationic actinide monoxides and dioxides from thorium to curium was carried out. A consistent set of metal-oxygen bond dissociation enthalpies, ionization energies, and enthalpies of formation, including new or revised values, was proposed. Preliminary studies of the energetics of actinide sulfides were also performed.

We continued to study the activation of methane and carbon dioxide as valuable C1 feedstocks, namely through the catalytic partial oxidation of CH₄ (POM reaction) using O₂, CO₂ or N₂O as oxidants. The production of syngas with the appropriate H₂/CO mol ratio of 2 and high conversion of methane was obtained over bimetallic lanthanide and actinide/nickel based oxide catalysts. A new route for obtaining the catalysts was developed - a molten salt route using eutectic potassium-lanthanides molten chloride salts. The best results were those obtained on cerium molten

salts and the main reaction products were always hydrocarbons which is a novelty over f-block elements catalysts.

We continued the investigation of the coordination chemistry of actinides and lanthanides based on O-and/or N-donor ligands of the azamacrocyclic and polypyrazolylalkane families. A new dianionic hexadentate N4O2-donor ligand was used as ancillary ligand to stabilize Y and La metal complexes of the type [MLCl]. The synthesis of Nd complexes bearing 3-(2-pyridyl)pyrazolylmethane ligands was initiated. The synthesis and characterization of new ionic liquids exhibiting luminescent properties and involving Ln complexes with beta-diketonate ligands was also performed.

The study of the energetics of organic, inorganic and organometallic molecules was continued and a database of the enthalpies of formation of organic compounds was made available on-line (www.therminfo.com). The experimental study of polyalkoxides of alkaline and alkaline-earth metals was initiated.

Collaborations with the Radiation Technologies: Processes and Products Group (Physics and Accelerators Unit) in the study of the gamma radiation effect on wastes, and with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems, continued.

Joint projects with the Research Unit "Glass and Ceramic for the Arts" (a collaboration between ITN, FBAUL and FCT/UNL) on provenance studies of Portuguese glasses, new lanthanide based fluorescent glasses, ruby glass and analysis of glazes in tiles were pursued.

A relevant part of the activity of the Group is the training of research students. Some of the group members are involved in undergraduate and post-graduate university courses. The financial support for the work is mainly from FCT, via research projects and PhD and Post-doc grants.

Research Team

Researchers

J. MARÇALO, Princ., Group Leader

J. BRANCO, Aux.

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J. M. CARRETAS, Aux.

C. C. L. PEREIRA, Aux., Contract

L. J. MARIA, Aux., Contract (Since Sep.)

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B. MONTEIRO, Post-Doc, FCT Grant (Mar.-Dec.)

Technical Personnel

A. CARVALHO

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Students

R. MELO, PhD student, FCT grant

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Gas-Phase Chemistry of Actinides and Lanthanides

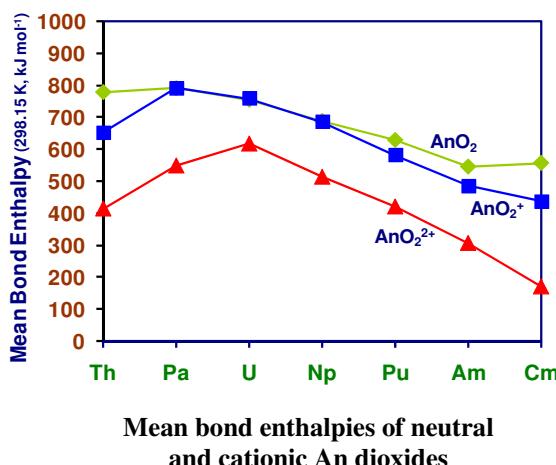
J. Marçalo, C. C. L. Pereira, J. P. Leal, J. M. Carretas, A. Pires de Matos,
A. P. Gonçalves¹, J. K. Gibson²

Objectives

The gas-phase chemistry of atomic and molecular actinide and lanthanide ions is studied in order to obtain thermodynamic, kinetic and mechanistic information that may enhance the fundamental knowledge of these elements. The experimental work is based on the use of advanced mass-spectrometry techniques, namely, LDI-FTICR/MS and ESI-QIT/MS. For the actinides, the explicit aims are to produce species with new ligations and properties, probe the role of 5f electrons in chemical bonding, and determine thermodynamic data for species of interest for condensed-phase processes. Parallel theoretical studies of selected actinide molecular ions are also carried out via collaborations to assist in the interpretation of experimental observations.

Results

The large amount of data that was gathered from our previous studies of actinide oxides from thorium to curium led to an overall assessment of the gas-phase energetics of neutral and singly and doubly charged cationic actinide monoxides and dioxides [1]. We evaluated the data from standard literature sources, tested and expanded the assessment of the known bond dissociation energies of neutral and singly-charged actinide monoxides carried out by J. K. Gibson some years ago, based on correlations with the electronic structures and energetics of the isolated metal atoms and ions, and provided correlations with condensed-phase thermochemistry. A consistent set of metal-oxygen bond dissociation enthalpies, ionization energies, and enthalpies of formation, including new or revised values, was proposed. We also proposed new estimates for the second ionization energies of the actinides from Th to Cm.



On the experimental side, we again used the FTICR/MS technique to probe this time the An-S ligation for An = Th, U and Cm [2,3]. We studied the reactions of the An⁺ metal cations with CS₂ and of the AnS⁺ species produced with selected neutral reagents. Estimates of the An metal-sulfur bond energies for the cationic and neutral monosulfides, and of the ionization energies of the neutral monosulfides could be obtained.

ESI of thorium and uranyl nitrates in water/methanol solutions generates several species in the negative ion mode which, depending on instrumental parameters or on deliberate CID, lead to different oxo- or hydroxo-containing ions [4]. The oxo ions bear special interest as the type of bonding of the oxo ligands determines the oxidation state of the metal centres.



ESI-QIT mass spectrometer
(Part of the National Mass Spectrometry Network – RNEM)

Published work

“Gas-Phase Energetics of Actinide Oxides – An Assessment of Neutral and Cationic Monoxides and Dioxides from Thorium to Curium”, J. Marçalo, J. K. Gibson, *J. Phys. Chem. A* 113 (2009) 12599–12606.

“Actinide Sulfide Ions in the Gas Phase: A Preliminary FTICR-MS Study of the Reactivity and Thermochemistry of ThS⁺ and US⁺”, J. Marçalo, C. C. L. Pereira, J. K. Gibson, *Actinides 2009*, S. Francisco, CA, USA, Jul. 2009.

“Actinide Sulfides in the Gas Phase: A Preliminary FTICR-MS Study of the Thermochemistry of Curium Sulfide”, C. C. L. Pereira, J. Marçalo, J. K. Gibson, *8th Inorganic Chemistry Conference - Sociedade Portuguesa de Química*, Curia, Oct. 2009.

“A Few Examples of the Current Research Work at the I.T.N.-Node of R.N.E.M.”, J. P. Leal, R. Melo, M. L. Botelho, J. Marçalo, I. Paiva, J. M. Carretas, C. C. L. Pereira, T. A. Gasche, *Annual Meeting of the Portuguese Mass Spectrometry Network*, Lisboa, Oct. 2009.

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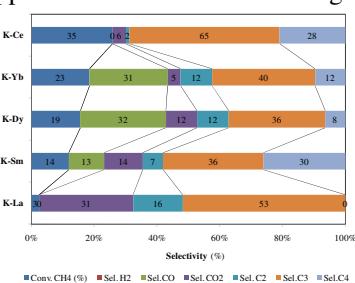
² Lawrence Berkeley National Laboratory (Berkeley, California, USA).

f-Block Elements as Catalysts

J. B. Branco, A. C. Ferreira, G. Lopes, T. A. Gasche, M. R. Correia¹, A. Rego², A. Ferraria², A. P. Gonçalves³

The main objective of this research is: (i) to study the f-block elements behaviour as catalysts or catalytic precursors, (ii) to develop new methods for the preparation of 4f and 5f nanostructured materials for catalytic purposes and (iii) to contribute for the resolution of key environmental issues.

We continued to study the activation and valorisation of methane and carbon dioxide as valuable C1 feedstocks, namely through the catalytic partial oxidation of CH₄ (POM reaction) using O₂, CO₂ or N₂O as oxidants. The catalysts were obtained by three routes: i) an intermetallic route, using LnCu₂ and LnNi₂ (Ln = from La to Yb) or AnNi₂ (An = Th, U) and ThCu₂ as bimetallic oxides precursors, ii) a sol – gel route (urea or citric acid methods) to obtain nanoparticles of bimetallic oxides and, recently, iii) a molten salt route using eutectic potassium-lanthanides molten chloride salts. Molten salts offer unique opportunities and alkali molten metal chlorides appear has a “new” and challenging group of catalysts for a number of applications. The production of syngas



with the appropriate H₂/CO mol ratio of 2 and high conversion of methane was obtained over the bimetallic nickel based oxide catalysts, cheaper materials with an activity and selectivity comparable to that of noble metal based catalysts, e.g. 5 wt. % M/Al₂O₃ (M-Rh, Pt). Taking into account the importance of NO_x as pollutants, it was established that the CH₄/N₂O molar ratio has a significant influence on the selectivity (decreases the selectivity to CO_x and increases the selectivity to hydrocarbons). The catalytic performance of the molten salts of the type KCl-LnCl (Ln = La, Ce, Pr, Sm, Gd, Dy, Yb) is clearly different and depends on the rare earth. The best results were those obtained on cerium

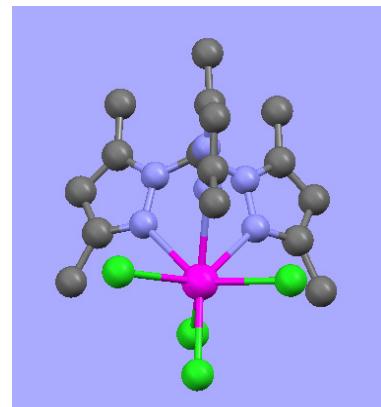
molten salts (Conv. = 35%, Sel. = 0, 5.7, 1.5, 64.6 and 28.2 % for CO, CO₂, C₂, C₃ and C₄, respectively). The main reaction products were always hydrocarbons (C₂, C₃ and C₄; Sel.C3 > 70%) which, to our knowledge, is a novelty over f-block elements catalysts.

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f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

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We continued the investigation of the coordination chemistry of actinides (Th and U) and lanthanides (Ln) based on O- and/or N-donor ligands, with potential interest in organic synthesis and catalysis, lanthanide/actinide separations and luminescence applications. Azamacrocyclic ligands have known a growing interest owing to their coordination properties and their range of applications, including metal mediated catalysis. A new dianionic hexadentate N₄O₂-donor ligand, 1,8-bis(methylene-di-*tert*-butylphenolate)-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane, was used as ancillary ligand to stabilize the large rare earth metal cations. Preliminary results with Y and La have shown that it is adequate to stabilize metal complexes of the type [MLCl]. The complexes have been fully characterized by ¹H NMR and ¹³C NMR, based on 2D-NMR experiments. Studies of the chemistry of Th, U and Ln with neutral ligands of the pyrazolylalkane family were pursued. Design and synthesis of new pyrazolylmethanes were performed, namely of bis- and tris-[3-(2-pyridyl)pyrazolyl]methane. The study of the synthesis of Ln complexes bearing these ligands and also the neutral “arm” 3-(2-pyridyl)pyrazole and its anionic counterpart 3-(2-pyridyl)pyrazolide was initiated using NdCl₃ and different reaction conditions. With the tris(3,5-dimethylpyrazolyl)methane (Tpm*) ligand, the x-ray crystal structure of the complex ThCl₄(Tpm*) was determined. Formation of cationic derivatives of the U complexes UCl₄(Tpm*) and UI₃(Tpm*)(THF) was investigated using AgBPh₄. Work involving the bis(3,5-dimethylpyrazolyl)methane ligand and UCl₄ and UI₃(THF)_x starting materials was also performed. The synthesis and characterization of new ionic liquids exhibiting luminescent properties in the visible region of the spectrum and involving Ln complexes was performed. Luminescent complexes of Eu with beta-diketonate ligands were synthesized in the form of tetrakis salts of the type NaEu(β-diketonate)_nCl_{4-n}. Two different β-diketones were used, β-naphtoyl trifluoroacetone (β-NTA) and dibenzoylmethane (Hdbm). The counter-ion was afterwards exchanged following the same strategy as for the ionic liquids involving organic fluorophores.



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Molecular Energetics of Organic, Inorganic and Organometallic Compounds

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The main objective of this research is to collect energetics data, rationalize it in a systematic way and explore connections between energetics and structure on molecules (both inorganic and organic compounds). Special importance was given to f-element compounds (both in solid state and in solution). To achieve this goal, lanthanide and actinide (organometallic and intermetallic), alkaline and alkaline-earth compounds, hydrocarbons and ionic liquids were studied. During 2009, an extended version of an empirical model for the prediction of the enthalpies of formation of hydrocarbons was published. Also, a database of the enthalpies of formation of organic compounds was made available on-line (www.therminfo.com). The nature of ionic liquids in the gas phase continued to be studied and the kinetics of some of the reactions where they are involved were investigated using FTICR/MS. The thermal properties of some ionic liquids were studied using thermal analysis techniques and the correspondent reactivity was explored using a QIT/MS apparatus. The study of polyalkoxides of alkaline and alkaline-earth metals took its first steps - synthesis and characterization of the compounds. Until now Na, K and Ca compounds with ethylene glycol were synthesized. The degradation/decomposition mechanism of gallic acid was elucidated by using pulse-radiolysis and mass spectrometry (QIT/MS). The gas-phase acidity measurements of methoxy di-substituted phenols were concluded.



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Glass Science with Applications in Archaeometry and Art Studies

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A. Pires de Matos is coordinating the research unit VICARTE - "Glass and Ceramics for the Arts", supported by FCT, with participants from ITN, FBAUL and FCT/UNL. Expertise on glass science is being developed, particularly in the synthesis of glasses with new properties and in chemical

characterisation of glasses for provenance studies.

In 2009 the Arcanum of Guilherme Stephens was studied. An attempt to

clarify the chemical nomenclature and glass jargon used by Stephens was made and the probable sources of the raw materials were investigated. The production methods and equipment used in the last quarter of the 18th century at Marinha Grande were studied. A few glass samples were reproduced using several compositions referred in the Arcanum to check the validity of the proposed nomenclature and to investigate the conditions used to obtain the colours. Micro-EDXRF and UV-Vis absorption spectrometry were used to characterize and compare laboratory reproduced samples with museum collection items seemingly attributable to the Stephens production period at Marinha Grande. Another research area is related with the development of glasses for artistic applications. Studies on luminescent glasses with rare earths have continued and application in art objects was made. Gold and copper ruby glasses were synthesized using gamma radiation for reduction of the metal ions and to improve nucleation of the metal nano-particles. A collaboration with the industry in this area has started. Studies of glazes in tiles using Raman spectroscopy were performed. With the same purpose, experiments to characterize glass by LIBS (Laser Induced Breakdown Spectroscopy) using a home-built system involving a Nd:YAG laser (ITN) and an optical fiber UV-Vis absorption spectrometer were continued.

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² Museu do Vidro, Marinha Grande.

Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems

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Membranes using polyethylene as backbone polymer and HEMA as grafting molecule, produced through irradiation on a ⁶⁰Co source, were synthesized and the corresponding properties extensively studied. New uses for these compounds were explored.

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